

NOVEL LIQUEFACTION SOLVENT: $\text{H}_2\text{O}-\text{H}_2\text{S}$

Virgil I. Stenberg, Robert D. Hei, Philip G. Sweeny, Jan Nowok

Department of Chemistry, University of North Dakota
Box 7185 University Station, Grand Forks, ND 58202

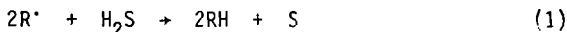
Warrack G. Willson

University of North Dakota Energy Research Center
University of North Dakota, Grand Forks, ND 58202

INTRODUCTION

The liquefaction solvent has two roles to fulfill: (1) a slurrying liquid for the coal which enables slurry compression into a continuous flow reactor, and (2) a hydrogen shuttler which enables the transfer of hydrogen atoms from H_2 or synthesis gas to the coal molecules. Additionally, the solvent serves as a medium for reducing gas and coal product dissolution.

We now wish to describe the use of $\text{H}_2\text{O}-\text{H}_2\text{S}$ as a substitute for organic slurrying solvents. The philosophy for doing so is that the water fulfills the role of the slurrying liquid and H_2S is the hydrogen atom donor. Since the first bond dissociation energy of water is 118 kcal/mole, rarely, if at all, would it be expected to react with carbon radicals. On the other hand, H_2S has the first bond dissociation energy of 93 kcal/mole and the second of 83 kcal/mole making it a good but not excellent hydrogen atom donor to carbon radicals (reaction 1). At the higher temperatures of conventional coal liquefaction reactors the thermodynamics would probably be more favorable. Reaction 2 has proven to be rapid at coal liquefaction temperatures and is



perhaps the principal advantage of H_2S over an organic solvent. The corresponding reaction for the organic solvent is usually slow. In organic liquefaction solvents, H_2S is known to enhance liquefaction yields, and it has been used for both coal and organic model compound reactions.

Water becomes supercritical at 374°C and its supercritical state has the potential of influencing the liquefaction processes in several ways: it (1) becomes a fine solvent for hydrocarbons (Fig. 3), (2) loses much of its ability to dissolve inorganic material (Fig. 2), (3) adds to the reaction pressure, and (4) becomes more ionic (acidic and basic) since the ionization constant increases by ca. 3 powers of ten (Fig. 3). If water is to be substituted for an organic slurrying liquid, the increase in reaction pressure

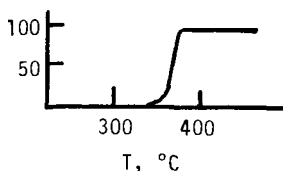


Fig. 1. Hydrocarbon solubility (wt %) in water

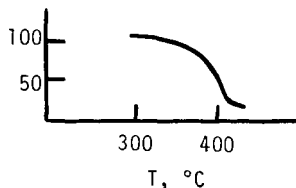


Fig. 2. Inorganic solubility (wt %) in water

(to ca. 5,000 psi) must be tolerated. Therefore, one must insist there be compensating factors for this pressure increase which more than make up for the cost of increased operating pressures. Batch autoclave data now indicate this is so. Indeed, water appears to have a positive effect on liquefaction yields in addition to its role as a slurrying liquid.

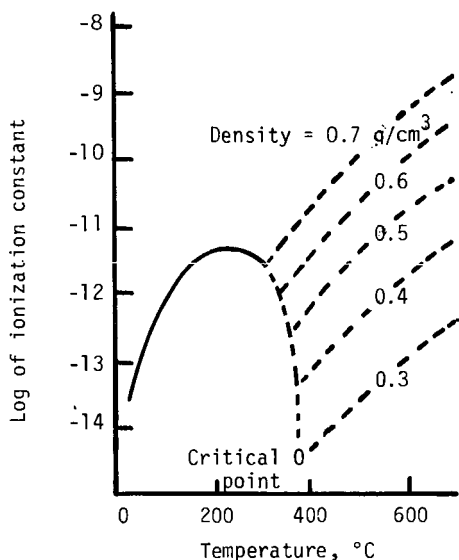


Fig. 3. Ionization constant of water in high-temperature fluids of various densities. The solid line is the experimentally determined curve for liquid water under its own vapor pressure. The estimated extrapolation of the curve to the critical point is shown as a dashed line. The other dashed lines shown calculated values of the constant for single-phase fluid water under sufficient pressure to maintain the indicated densities.

RESULTS AND DISCUSSION

The data of Table 1 compare the H_2O - H_2S results along with those using (1) a petroleum-coal based organic solvent, anthracene oil (A04) together with a solvent refined coal middle distillate from the demonstration plant at Tacoma, Washington (SRCMD) and (2) dihydropyrene (DHP), a reputedly excellent hydrogen donor solvent. Three ranks of coals are represented in the data.

Water with synthesis gas outperform A04-SRCMD with synthesis gas for the conversion of two coal samples into volatile materials at the conditions used, cf. runs 5 vs. 7 and 14 vs. 16. The presence of a small amount of H_2S enhances the as-defined yields whether in water, cf. runs 1 vs. 2, 7 vs. 8, 16 vs. 17, 21 vs. 22, 26 vs. 27 and 31 vs. 32 or in an organic solvent, cf. 5 vs. 6, 12

vs. 13, 14 vs. 15, 19 vs. 20, 24 vs. 25 and 34 vs. 35. The reactions which had the temperature programmed from 300°C to 500°C using H_2O-H_2S and synthesis gas gave the best of the aqueous- H_2S conversion yields, cf. runs 8 vs. 9, 17 vs. 18, 22 vs. 23, 27 vs. 28 and 32 vs. 33. Synthesis gas is superior to pure H_2 (980 psig), cf. runs 3 vs. 5 and 12 vs. 14.

The philosophy behind the temperature programmed reactions was the belief that the thermally produced, coal-derived radicals would be formed in a more controllable fashion, i.e., in a more steady, slower rate, within the coal-water slurry than with a sudden thermal jump to a preselected reaction temperature. The latter is assumed to momentarily deplete the hydrogen donor capacity of the solvent system at least in the vicinity of the thermal reaction events. In the case where water is the principal solvent, the hydrogen donor capacity is the H_2S concentration. The consequence of this depletion is the occurrence of retrograde reactions which result in lower conversions.

The dihydrophenanthrene (DHP) runs gave better conversions than either water or A04-SRCMD given otherwise the same experimental conditions. However, DHP decomposes to the extent of 11% at 420°C at 30 minutes, and the non gaseous products are solids rather than liquids as they are with the water runs. The water runs were the easiest to separate from the product slurry. The distillation was complete in ca. 3 hours with the water runs whereas it took from 5-7 hours to get to constant weight with the organic solvent-based runs. The oil separated by gravity from the water in the water based run distillates.

In summary, the H_2O-H_2S solvent runs with various ranks of coals give respectable yields of total volatile materials at 420°C and with temperature programming the reactor from 300° to 500°C, the yields were as good if not better than using one of the best of hydrogen donor model compound solvents. The H_2S concentration the programming rates or ranges have not been optimized.

ACKNOWLEDGMENT

We are grateful to the U.S. Department of Energy for the financial support of this study.

REFERENCES

1. (a) Stenberg, V.I.; Baltisberger, R.J.; Ogawa, T.; Raman, K., and Woolsey, N.F., Hydrogen Sulfide Catalysis of Low Rank Coal Liquefaction, ACS Fuel Division Preprints, 1982, 27(3-4), 22. (b) Stenberg, V.I.; Raman, K.; Srinivas, V.R.; Baltisberger, R.J., and Woolsey, N.F., H_2S as a Promotor for the Water Gas Shift Reaction, *Angew. Chemie, Int. Ed., Engl.*, 1982, 21(8), 619. (c) Sondreal, E.A.; Wilson, W.G., and Stenberg, V.I., Mechanisms Leading to Process Improvements in Lignite Liquefaction Using CO and H_2S , *Fuel*, 1982, 61, 926.
2. (a) Gatsis, J.G., U.S. Patent No. 3 503 863 (1970). (b) Bearden, R., Jr. and Albridge, C.L., U.S. Patents Nos. 4 077 867 (1978), 4 094 765 (1978) and 4 149 959 (1979). (c) Lambert, J.M., Jr., *Fuel*, 1982, 61, 777. (d) Abdel-Baset, M.B. and Ratcliffe, C.T., Preprints, Div. of Fuel Chemistry, Amer. Chem. Soc., 1979, 25(1), 1. (e) Baldwin, R.M. and Viciguerra, S., *Fuel*, 1983, 62, 498. (f) Okutani, T., Yokoyama, S. and Maekawa, Y., *Ind. Eng. Chem. Process Des. Dev.*, 1983, 22, 306.
3. (a) Josephson, J., *Environ. Sci. Technol.*, 1982, 16(10), 548A. (b) Mackay, M.E., and Paulaitis, *Ind. Eng. Chem. Fundam.*, 1979, 182, 149. (c) Johnston, K.P., Ziger, D.H., and Eckert, C.A., *Ibid.*, 1982, 21, 191. (d) Procaccia, I., and Gitterman, M., *AIChE Journal*, 1983, 29(4), 686. (e) Johnston, K.P., and Eckert, C.A., *ibid.*, 1981, 27(5), 774.
4. Krauskopf, K.B., "Introduction to Geochemistry", McGraw-Hill Book Company, New York, NY, p. 496.

Table 1. The Conversion of Coals in H_2O-H_2S and A04-SRCMD

	Lignites	Reducing gases ²	Temperature, °C	Sovent	Conversion, %
1	Indianhead (Zap 1)	$CO-H_2$	420	H_2O	37.4
2	Indianhead	$H_2S-CO-H_2$	420	H_2O	42.8
3	Big Brown (BB1)	H_2	420	A04-SRCMD	35.2
4	Big Brown	H_2S-H_2	420	A04-SRCMD	35.3
5	Big Brown	$CO-H_2$	420	A04-SRCMD	42.5
6	Big Brown	$H_2S-CO-H_2$	420	A04-SRCMD	48.1
7	Big Brown	$CO-H_2$	420	H_2O	43.7 ± 2.0
8	Big Brown	$H_2S-CO-H_2$	420	H_2O	48.9 ± 1.2
9	Big Brown	$H_2S-CO-H_2$	300-500	H_2O	71.0
10	Big Brown	$CO-H_2$	420	DHP	50.7 ± 4.4
11	Big Brown	$H_2S-CO-H_2$	420	DHP	65.3 ± 3.5
12	Beulah (B3)	H_2	420	A04-SRCMD	22.2
13	Beulah	H_2S-H_2	420	A04-SRCMD	29.3
14	Beulah	$CO-H_2$	420	A04-SRCMD	30.1
15	Beulah	$H_2S-CO-H_2$	420	A04-SRCMD	40.5
16	Beulah	$CO-H_2$	420	H_2O	33.8 ± 1.0
17	Beulah	$H_2S-CO-H_2$	420	H_2O	36.8 ± 0.3
18	Beulah	$H_2S-CO-H_2$	300-500	H_2O	51.6 ± 1.1
19	Beulah	$CO-H_2$	420	DHP	46.6
20	Beulah	$H_2S-CO-H_2$	420	DHP	53.3 ± 3.0
<u>Subbituminous coals</u>					
21	Decker (DEC 1)	$CO-H_2$	420	H_2O	38.6 ± 0.4
22	Decker	$H_2S-CO-H_2$	420	H_2O	40.6 ± 1.5
23	Decker	$H_2S-CO-H_2$	300-500	H_2O	52.3 ± 0.7
24	Decker	$CO-H_2$	420	DHP	48.4
25	Decker	$H_2S-CO-H_2$	420	DHP	60.2 ± 8.0
26	Absaloka (ABS 1)	$CO-H_2$	420	H_2O	29.6 ± 0.3
27	Absaloka	$H_2S-CO-H_2$	420	H_2O	34.1 ± 1.1
28	Absaloka	$H_2S-CO-H_2$	300-500	H_2O	51.0 ± 0.7
29	Absaloka	$CO-H_2$	420	DHP	N.A.
30	Absaloka	$H_2S-CO-H_2$	420	DHP	49.6 ± 3.5
<u>Bituminous coals</u>					
31	Powhattan (POW 1)	$CO-H_2$	420	H_2O	24.7 ± 0.4
32	Powhattan	$H_2S-CO-H_2$	420	H_2O	30.5 ± 0.8
33	Powhattan	$H_2S-CO-H_2$	300-500	H_2O	41.9 ± 0.7
34	Powhattan	$CO-H_2$	420	DHP	43.5
35	Powhattan	$H_2S-CO-H_2$	420	DHP	51.6 ± 3.5

The experimental conditions are: reaction time, 1 hour; H_2S , 250 psig; CO , 490 psig; H_2 , 490 psig; coal, 1 gram; and water, 1 gram. When H_2 alone was used, its pressure was 980 psig. The conversion yields were determined by distilling the volatile material (gases and liquids) from the reactor contents at 250°C at 1 Torr for 5 hours (H_2O) and 7 hours (A04-SRCMD). The coal samples are cited from the mine site: Indianhead from the Indianhead Mine at Zap, North Dakota; Big Brown from the Big Brown Mine at Fairfield, Texas; Beulah from the South Beulah Mine, Beulah, North Dakota; Decker from the Decker Mine at Big Horn, Montana; Absaloka from the Absaloka Mine at Sarpy Creek, Montana; and Powhattan from the Powhattan Mine at Belmont, Ohio.